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13. ABSTRACT (Maximum 200 words)  Nanocrystalline composites of Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> have been synthesized through four different processes and evaluated in terms of their densification and ability to retain the metastable tetragonal zirconia phase. The physical stabilization of the tetragonal phase is dependent primarily on the microstructure of the material which is a strong function of the powder preparation method. Significant stabilization of the tetragonal phase after thermal treatments at 1200°C was achieved with the colloidal processing approach. The results show that the high degree of phase stabilization in this sample may have come from the creation of a three-phase composite with the ZrO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , and closed pores acting as mutually insoluble phases thereby reducing grain growth and preventing the zirconia phase transformation. Future research will address the relationships between microstructure and processing more thoroughly through electron microscopy with the goal of minimizing the requirement on Al <sub>2</sub> O <sub>3</sub> content. In addition, methods for forming coatings from these powders with phase stabilization will be investigated.				
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"Processing of  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  Nanocomposites for Thermal Barrier Coatings"

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Materials which are to be used as thermal barrier coatings must meet several criteria, including low thermal conductivity, high resistance to thermal cycling, a reasonably high thermal expansion coefficient, and resistance to environmental degradation. Partially stabilized tetragonal zirconia has been studied extensively as a thermal barrier coating due to its ability to meet many of these criteria. However, yttria stabilized zirconia can undergo leaching of the yttria under moderate temperatures with severe consequences to the phase stability and resistance to thermal cycling<sup>1,2</sup>. One proposed method of overcoming this difficulty is to stabilize the tetragonal phase physically rather than chemically. Physical stabilization requires that the size of the zirconia grains be kept below approximately 30 nm. This can be accomplished by creating a composite material of mutually insoluble phases which will increase the diffusion distances and reduce the grain growth kinetics. One system of particular interest for this application is the  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  system because the phases are nearly completely insoluble in each other and both components are extremely refractory. However,  $\text{Al}_2\text{O}_3$  has a significantly higher thermal conductivity than  $\text{ZrO}_2$  so that an additional goal of this project is to minimize the amount of alumina required for complete phase stabilization of the tetragonal zirconia phase. This project was concerned with the design and evaluation of four different synthesis methods for nanocrystalline  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  thermal barrier materials<sup>3</sup>. These procedures were then evaluated in terms of their ability to synthesize materials which retain the tetragonal zirconia phase after extended heat treatments. The four synthesis methods, (coprecipitation, butoxide, nitrate, and colloidal) are described along with the significant observations made during this project.

Coprecipitation:

Coprecipitation is well known as a simple way to obtain molecular mixing of components and nanometer sized grains. In the case of  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$ , the coprecipitation process (Figure 1) results in a metastable amorphous mixture of the hydroxides which crystallizes at temperatures between 500 and 800°C, depending on the volume fraction of alumina. Coprecipitation has been widely used to produce nanocrystalline yttria and calcia doped zirconia particles with excellent sinterability and homogeneity. Similarly, the 5 and 20 vol%  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  particles we produced via coprecipitation showed excellent sinterability and achieved greater than 90% density by 1200°C (Figure 2). Unfortunately, the sintering resulted in rapid grain growth and complete

transformation of the tetragonal phase to the monoclinic phase at temperatures below 1200°C. This transformation resulted in large scale cracking of the material as it approached full density. The rapid densification and the concomitant grain growth and transformation suggest that a dense coating would be difficult to keep as a tetragonal phase without significantly more alumina than is desirable from a thermal conductivity standpoint. In addition, although a dense ceramic is generally desirable for bulk specimens, it is not desirable for a thermal barrier coating which will display improved mechanical and thermal properties when it is less than fully dense.

#### Butoxide and Nitrate Processes:

In an effort to create different microstructures, which would hopefully display improved resistance to densification and phase transformation, alternate synthesis methods were attempted. In these processes a commercial zirconia sol, obtained from Alfa Aesar, Inc., was used as the starting material and the alumina was added in two different ways. Conceptual drawings of the goals of these processes are shown in Figure 3 and the synthesis procedures are shown in Figure 4 for the butoxide and nitrate processes. The butoxide process was designed to produce a coating of alumina on the zirconia particles while the nitrate process would hopefully produce more discrete  $\text{Al}_2\text{O}_3$  particles in close proximity to the zirconia particles. Although the sinterability of these materials was low, with only 60-65% of theoretical density obtained for these processes with 50 vol%  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$ , the phase stabilization was quite poor such that specimens sintered for 2 hours at 1200°C were mostly monoclinic.

#### Colloidal Process:

The colloidal process, shown in Figure 5, gives intimate mixing of  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  particles rather than molecular scale mixing like that obtained via coprecipitation. This process yields the highest degree of tetragonal stabilization with the 50 vol%  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  displaying only trace amounts of the monoclinic phase after 12 hours at 1200°C. The degree of stabilization decreases with decreasing amounts of alumina however this process has not been optimized sufficiently to determine a lower limit for complete stabilization of the tetragonal phase. The density of the sintered compacts is generally between that of the butoxide and nitrate processed powder and the coprecipitated powder, but the closed pore volume of the colloiddally prepared specimens is two to three times that of the butoxide and nitrate prepared specimens. This suggests that in effect a three-phase composite is being constructed through this process with alumina, zirconia, and the porosity forming the mutually insoluble phases. Finally, these samples appear to be quite stable to extended heat treatments as shown in Figure 6, with the densities of samples sintered for 2 hours being nearly identical to samples which have been sintered for 12 hours. Attempts were made to increase the density of the pellets by cold isostatic pressing the pellets prior to sintering. Although final densities were improved, the percentage of tetragonal phase retained was decreased as well. A comparison of the nitrogen isotherms of the colloiddally prepared samples and the coprecipitated samples can give some insight as to the source of the closed porosity observed in these samples. Figure 7 shows the normalized adsorption-desorption isotherms of the coprecipitated and colloiddally prepared 20 vol%  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  samples. The large hysteresis observed in the colloiddally prepared sample is typical of "ink bottle" pores whereas the smaller hysteresis at higher  $P/P_o$  values in the coprecipitated powders is more typical of interparticle porosity. The large fraction of closed pores in the colloiddally

prepared samples is believed to come from the rapid closing of the necks of these ink bottle pores during sintering. This would create a large fraction of closed porosity which would significantly retard further densification and grain growth, allowing the tetragonal phase to be retained.

#### Conclusion:

The microstructure of the material appears to be extremely important in preventing grain growth and stabilizing the tetragonal phase. The differences in the methods of adding the alumina phase to the zirconia provided striking differences in degree of phase stabilization, sinterability, and pore volume. The best material, obtained by the colloidal process, may be thought of as a ternary composite with zirconia, alumina, and porosity as mutually insoluble phases. Further investigations involving high resolution electron microscopy, transmission electron microscopy, and scanning electron microscopy are planned to further elucidate the processing, microstructure, and phase stabilization relationships so that these materials can be optimized both in terms of their tetragonal phase stability and their thermal resistivity. In parallel with this microstructural analysis will be the development of processing parameters to turn these powders into coatings while maintaining phase stability with a minimal amount of  $\text{Al}_2\text{O}_3$ . Thermal spraying and other ceramic coating techniques will be attempted to further determine the structure-property relations in these  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  composite structures.

#### References:

1. M. Watanabe, S. Iio, and I. Fukuura, "Aging Behavior of Y-TZP" Science and Technology of Zirconia II, Advances in Ceramics, Vol. 12, 391-398, (1983).
2. K. Tsukuma, Y. Kubota, and T. Tsukidate "Thermal and Mechanical Properties of  $\text{Y}_2\text{O}_3$ -Stabilized Tetragonal Zirconia Polycrystals" Science and Technology of Zirconia II, Advances in Ceramics, Vol. 12, 382-390, (1983).
3. M. Panchula, J. Ying, L. Kurihara, and V. Provenzano, "Processing of  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  Nanocomposites for Thermal Barrier Coatings" in preparation.
4. Private communication with Naval Research Laboratory collaborator, Dr. Virgil Provenzano.

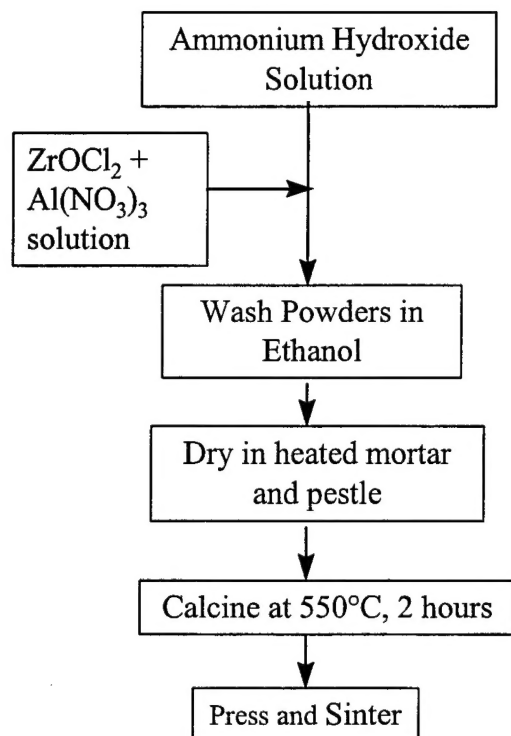


Figure 1. Synthesis process for coprecipitated  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  particles.

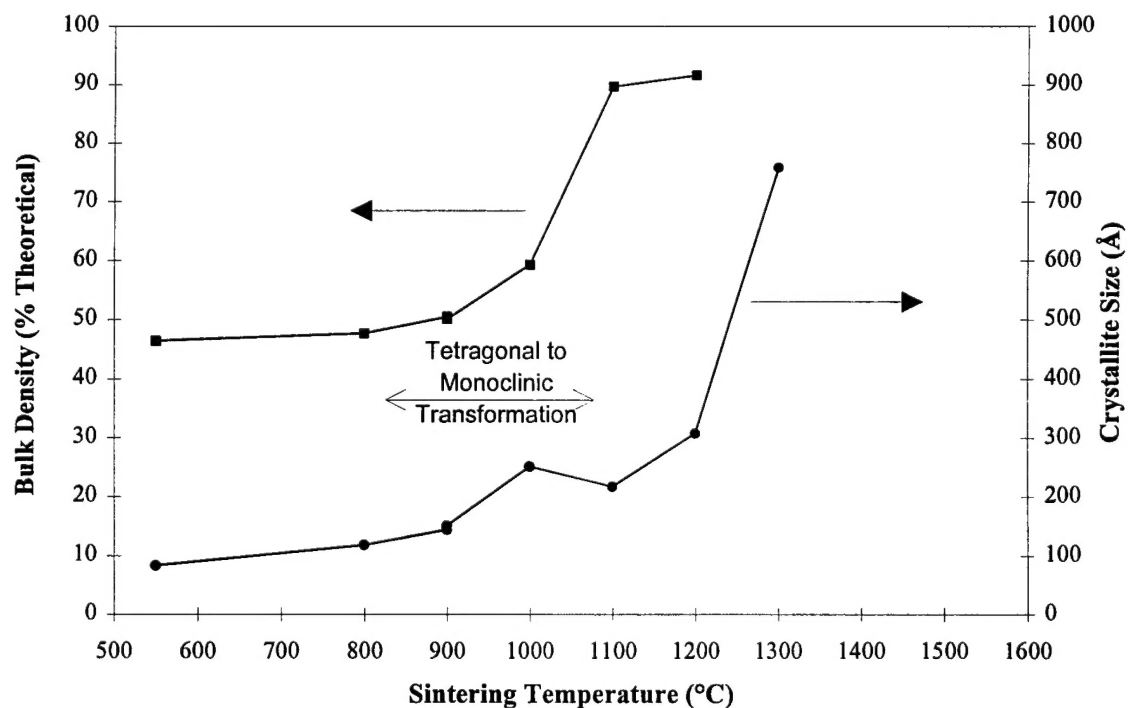
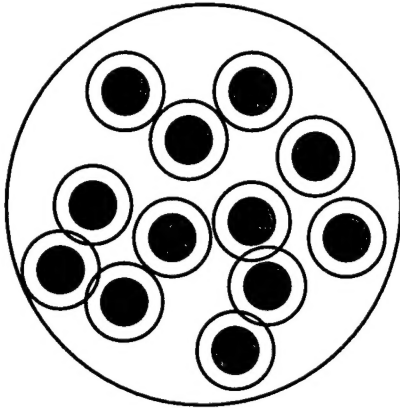
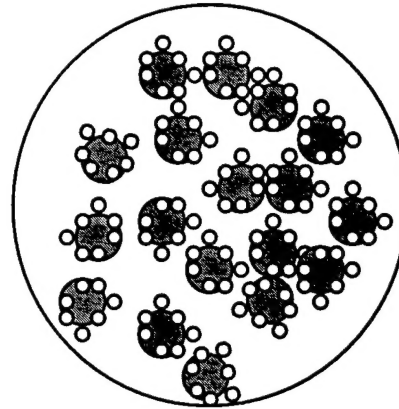


Figure 2. Density of 5 vol%  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  nanocomposite pressed at 88MPa and cold isostatically pressed at 400MPa and sintered for two hours.

A)

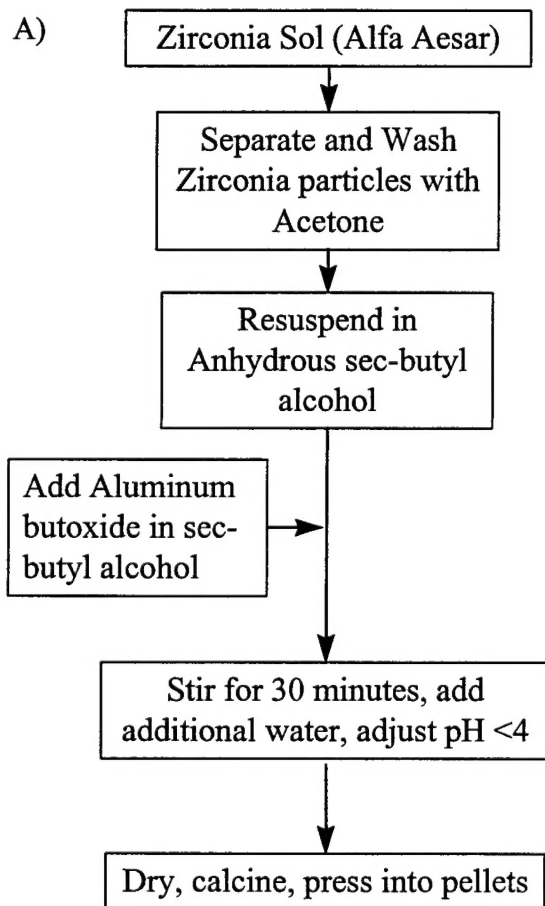


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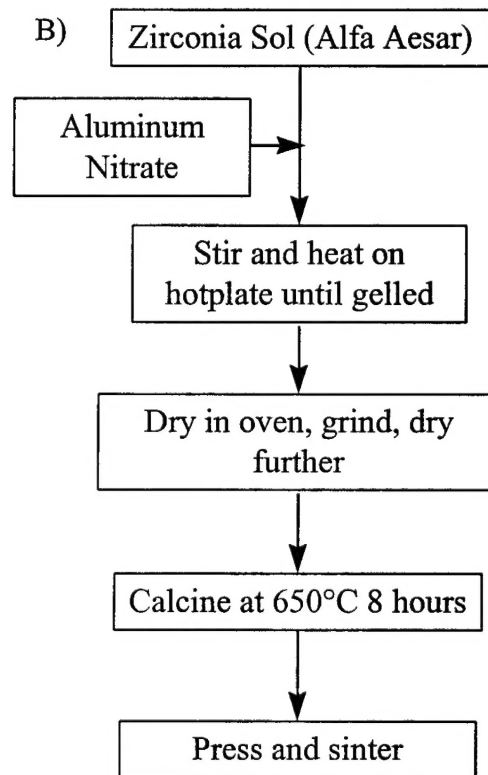


**Figure 3.** Microstructural design goals for the A) butoxide process and B) the nitrate process the dark regions are the zirconium particles while the light regions are alumina.

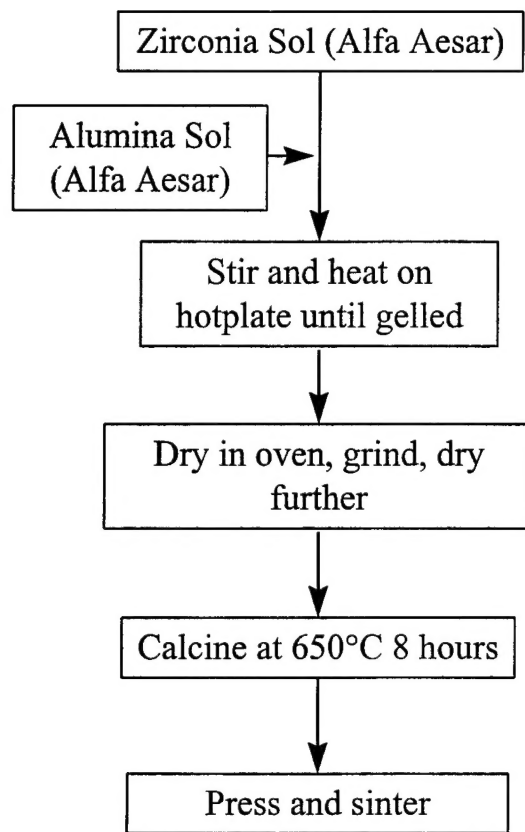
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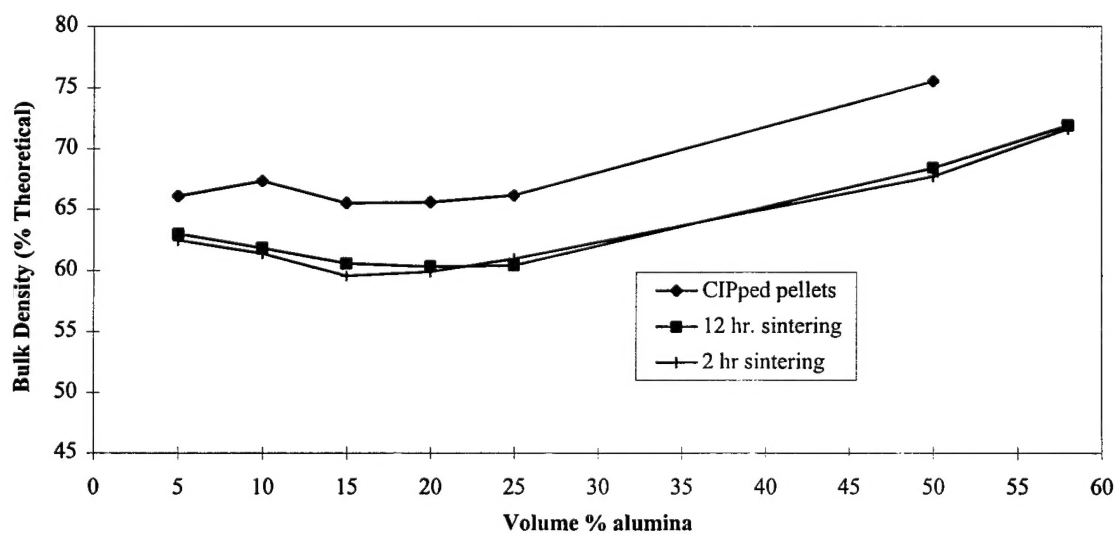
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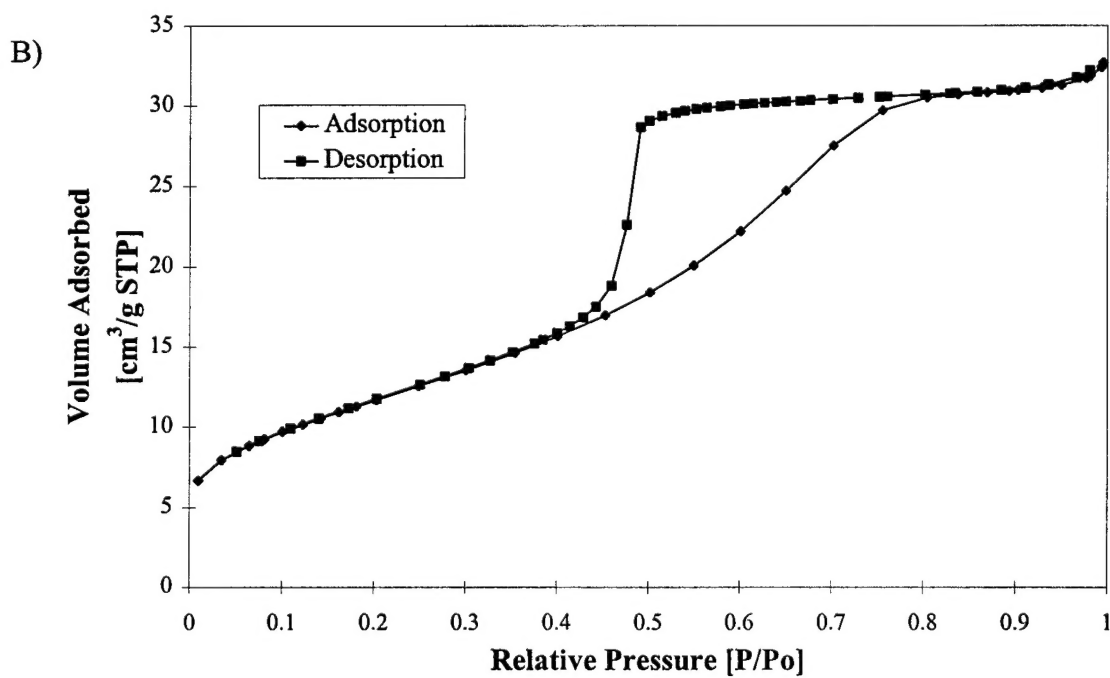
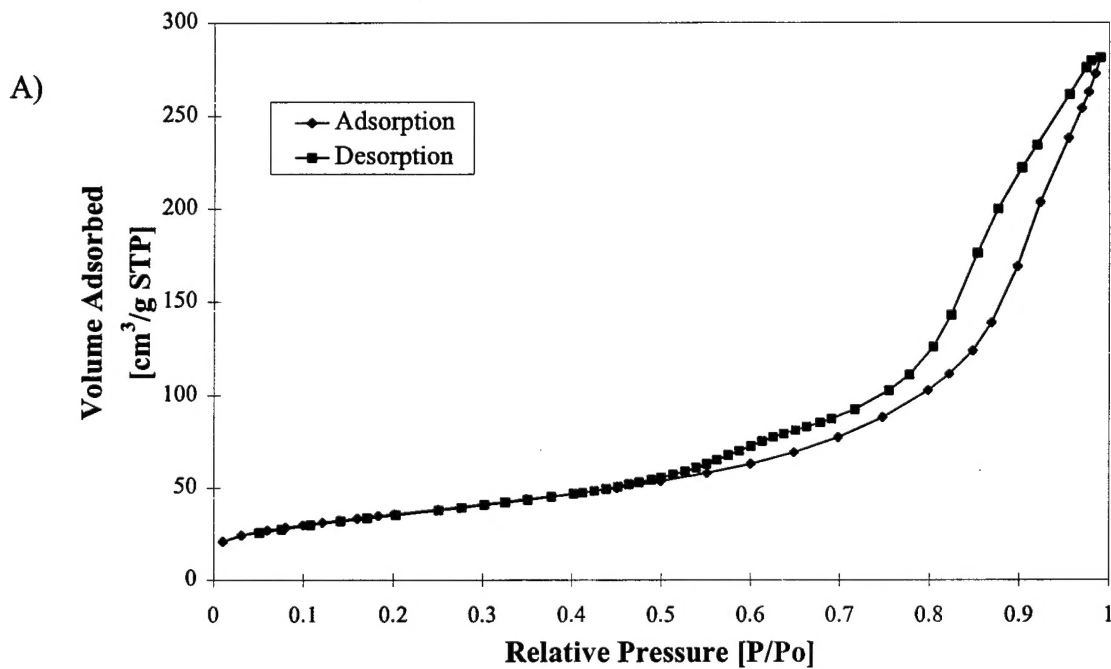
**Figure 4.** Synthesis methods for A) butoxide process and B) nitrate process.



**Figure 5.** Synthesis procedures for colloiddally prepared samples<sup>4</sup>.



**Figure 6.** Densities of colloiddally prepared powders after sintering at 1200°C.



**Figure 7.** Nitrogen adsorption-desorption isotherms for A) coprecipitated and B) colloiddally prepared samples with 20 vol% alumina.